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To: Joe Garman	**Date:** October 16, 1997
From: Cindy Boswell	

Subject: pH in Aqueous Solution Analysis

Objective

The purpose of this study was to:

A. assess the variability in results of a currently available method of testing pH in an aqueous solution,

B. determine if rinsing of the glass tubing results in different analytical results, and

C. determine the sample size necessary to obtain reliable results based on the variation observed.

Procedure

Mainstream whole smoke is collected from a cigarette as the smoke is drawn into impinger traps with each trap containing 50mL of degassed water. The traps are connected to a single port on a Filtrona smoking machine. After smoke collection is complete, the trap contents and the Cambridge filter are combined and the pH is determined at the 15th minute after smoking. This study was conducted using IM#16 samples, over a period of 3 days, with 10 replicate cigarettes tested on each day. Of the 10 cigarettes tested each day, the first 5 were tested as above, while for the remaining 5 samples, the bent tubing of the apparatus was also rinsed into the water solution.

Variability of the Results

The following results were obtained:

| Date		pH (Unrinsed)	pH (Rinsed)	Aggregate Date
10/8		5.349	5.330	
		5.369	5.360	
		5.354	5.342	
		5.360	5.355	
		5.320	5.369	
	Average	5.350	5.351	5.351
	Stand. Dev.	0.019	0.015	0.016
10/9		5.356	5.363	
		5.299	5.376	
		5.332	5.416	
		5.326	5.331	
		5.321	5.359	
	Average	5.327	5.369	5.348
	Stand. Dev.	0.021	0.031	0.033
10/10		5.376	5.353	
		5.352	5.374	
		5.379	5.364	
		5.313	5.353	
		5.299	5.339	
	Average	5.344	5.357	5.350
	Stand. Dev.	0.036	0.013	0.027
	Global Average	5.340	5.359	5.350
	Global Stand. Dev.	0.027	0.021	0.025

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Difference between Methods (Rinsed vs. Unrinsed Tubing)

Analysis of variance indicated that there were no significant effects due to day, puff volume, or the results of the pH7 buffer check but that there was a difference between the rinsed & unrinsed methods. This difference is very slight (5.340 for unrinsed vs. 5.359 for rinsed), but because the data had such low variability within each method (0.027 standard deviation for unrinsed and 0.021 standard deviation for rinsed), the difference between the 2 averages indicated the results were different. The box plot below illustrates this difference.

Categorized Plot for Variable: PH
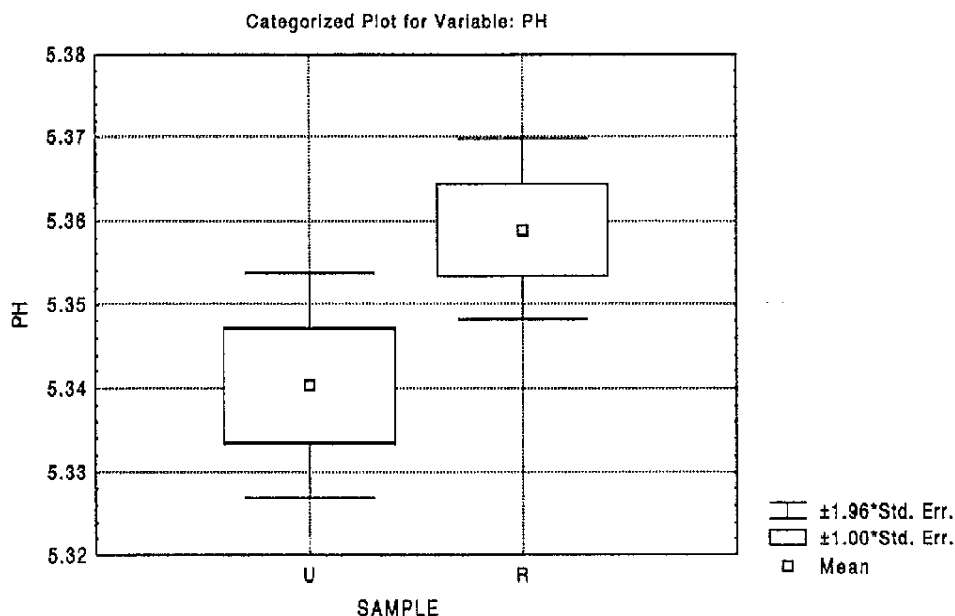
The real difference between the 2 methods, however, is revealed in the 2nd day of testing as seen below.

Categorized Plot for Variable: PH

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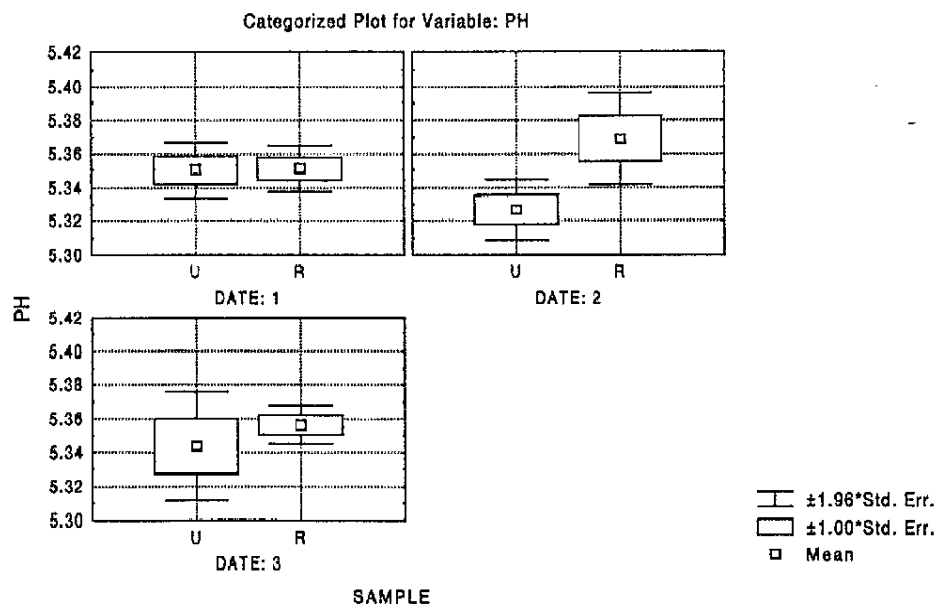
Sample Size Determination

Assuming, based on these results, that the recommendation is to continue the method with the rinsing step, the variation of the data from this procedure indicate that a sample size of 5 is sufficient to estimate the mean to within ±0.027pH with a 95% confidence level.

The standard deviation of all 15 data points of the "rinsed" method was 0.021. However, a more conservative estimate of the population standard deviation was used as the "worst case." In examining the 15 data points, we actually have 3 sets of 5 results. One could also combine these 3 sets of 5 results to obtain 3 possible sets of 10 results (Day 1 & Day 2, Day 1 & Day 3, Day 2 & Day 3). Of these 6 sets of results, the largest standard deviation obtained was 0.031 (Day 2 alone). Using this estimate of the population standard deviation, a 95% confidence level, and a sample size of 5, the width of the confidence interval is 0.054 or ±0.027. The following formula was used for this computation:

$$\text{Confidence interval} = \text{mean} \pm 1.96 \frac{0.031}{\sqrt{5}} = \text{mean} \pm 0.027$$

Using a sample size of 10 would estimate the mean to within ±0.019pH as shown below.

$$\text{Confidence interval} = \text{mean} \pm 1.96 \frac{0.031}{\sqrt{10}} = \text{mean} \pm 0.019$$

cc: Frank Hsu
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